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Effect of starting material on normal-pressure synthesis of 124 superconductor $Y_{1-x}Ca_xBa_2Cu_4O_8$

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Successful synthesis of the 124 high-T_c superconductor $Y_{1-x}Ca_xBa_2Cu_4O_8$ at ambient oxygen pressure is reported. A solid-state reaction technique using Cu(I)I instead of the conventional Cu(II)O in starting materials has been found to be effective for the normal oxygen-pressure synthesis of $YBa_2Cu_4O_8$ as well as calcium-substituted $Y_{1-x}Ca_xBa_2Cu_4O_8$. It was found that careful attention must be paid in preparing high-quality $Y_{1-x}Ca_xBa_2Cu_4O_8$. The chemical state of the initial calcium compound was a critical factor in the successful synthesis of $Y_{1-x}Ca_xBa_2Cu_4O_8$ at ambient oxygen pressure. © *1998 Chapman & Hall*

1. Introduction

The 124 high-temperature (high-T_c) superconductor $YBa_2Cu_4O_8$ (Y124) was first discovered as a defect structure in partly decomposed $YBa_2Cu_3O_x$ (Y123) powders [1] and in inhomogeneous Y123 thin films [2, 3]. The first synthesis of this superconductor in bulk phase was carried out at high oxygen pressures (oxygen-HIP) ranging from 40 MPa (1040 °C [4]) to 3.5 MPa (930 °C [5]). This superconducting material is of great interest because its oxygen content is thermally stable during heating and cooling up to 850 °C and the well-known tetragonal–orthorhombic phase transition during cooling in the most extensively researched Y123, is absent [4], which greatly benefits applications. For example, in the case of fabricating bulk superconducting materials, the feed of oxygen during heat treatment would be unnecessary and microcracks caused by the oxygen-induced phase transition could be avoided. The most promising application, we believe, may be the realization of a copper-sheathed superconducting wire, because heat treatment in oxygen is not a necessity and thus the oxidization of copper due to processing in oxygen could be avoided. The possibility of copper-sheathed wires could be seen from Karpinski's work which reported that $YBa_2Cu_4O_8$ is thermally stable even in argon up to 700 °C. Its low T_c of 80 K is reported to be enhanced to 90 K by 10% substitution of calcium for yttrium using the oxygen-HIP technique [6–8]. Nevertheless, for practical uses, large quantities, as well as simple preparation, are demanded, which cannot be satisfied by the high-pressure technique.

Up to now, tremendous effort has been made to synthesize the unsubstituted Y124 at ordinary oxygen pressures [9–36]. Many groups have succeeded in preparing high-purity samples. However, there are fewer reports on calcium-substituted Y124 despite its considerably higher T_c. It has been synthesized at normal pressures by the use of solution-based sol–gel techniques [24, 37], which are complicated and require delicate techniques. Ohara *et al.* [38] then reported a simple solid-state reaction method for synthesizing $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$, being characterized by adding 50 wt % Ag_2O to the superconducting compound to produce a T_c (onset) of 90 K and a T_c (zero resistance) (T_{c0}) of 77 K. Nevertheless, the use of a large quantity silver limits its application in many practical uses and, besides, in these normal-pressure synthesis reports the sample's thermal stability (a feature clarifying the 124 superconductor from the 90 K superconductor $YBa_2Cu_3O_x$ (Y123 phase), was not clear. This demands clarification because the inclusion of Y123 would be an obstacle to fabricating copper-sheathed wires.

Matsui *et al.* [39] investigated the effect of metal-substitution on the crystal structures of Y124 by electron diffraction and high-resolution transmission electron microscopy. They reported that 5–10% substitution of calcium for yttrium using a conventional solid-state reaction preparation made Y124 structure unstable and tended to promote the 123 phase formation. This may explain the fewer reports of synthesis of the calcium-substituted Y124 despite its greater interest than $YBa_2Cu_3O_x$ from the viewpoint of application.

We have developed a novel solid-state reaction method for synthesizing Y124 at ambient oxygen pressure without the use of a reaction-rate enhancer or sophisticated heat treatments [34]. This method features the use of Cu(I)I instead of the conventional Cu(II)O for calcination. Other than the conventional Cu(II)O with copper in a chemically bonded state of

Cu(II), the Cu(I) in Cu(I)I may actively react with the other components to form the Y124 superconductor. It has been confirmed that iodine evaporated completely in oxygen in the reaction. We have attempted to synthesize the 90 K superconductor $Y_{1-x}Ca_x Ba_2Cu_4O_8$ and have found that the state of the initial calcium compound is also critical to the synthesis. In this paper, the synthesis of $Y_{1-x}Ca_xBa_2Cu_4O_8$ ($x = 0.05$, 0.1) at ambient oxygen pressure, and the influence of the initial copper and calcium on the sample preparation are reported.

2. Experimental procedure

The $Y_{1-x}Ca_xBa_2Cu_4O_8$ compounds were prepared by a solid-state reaction process as detailed below. Calcium compounds of $Ca(NO_3)_2 \cdot 4H_2O$ (99.9%), $Ca(NO_3)_2 \cdot 4H_2O$ (99.9%) dissolved in acetone, and dried CaO (99.99%), were mixed with powders of Y_2O_3 (99.99%), $Ba(NO_3)_2$ (99%) and CuI (95%) according to the stoichiometric ratio of $Y_{1-x}Ca_xBa_2Cu_4O_8$ with $x = 0$, 0.05, 0.1 respectively. $Ca(NO_3)_2 \cdot 4H_2O$ has been usually used in preparing $Y_{1-x}Ca_xBa_2Cu_4O_8$ [24, 37, 38] for its steady property in air. The mixture was heated at 815 °C for 1 d, then ground and pelletized using a uniaxial pressing of 5000 kg cm^{-2}, sintered at 850 °C twice for 2 d, then subsequently cooled to room temperature (100 °C h^{-1}). All heating and cooling was carried out under flowing oxygen at a rate of ~100 cm^3 min^{-1}. Iodine evaporated during calcination was collected at the outlet by water and ethanol. For resistive and susceptibility measurements, some of the samples were shaped into rectangular bars of ~9 mm × 3 mm × 0.4 mm before the last sintering.

The superconductivity was investigated by the conventional four-probe resistivity and the d.c. magnetic susceptibility measurements with a SQUID susceptometer (Hoxan HSM-2000). In the former measurement, electrodes were formed on the sample surface by evaporating silver and the lead-in wires were attached to the electrodes using silver paste. In the magnetic susceptibility measurement, a d.c. magnetic field of 10 Oe was used and the Meissner susceptibility data were measured in field-cooling mode for the long rectangular samples. The quality of the samples was further evaluated by X-ray (Cu$K\alpha$ radiation) powder diffraction (XRD) and thermogravimetric (TG) measurements. For TG measurements, samples were heated at a rate of 10 °C min^{-1} in air.

3. Results and discussion

Fig. 1 shows the XRD patterns for $YBa_2Cu_4O_8$ and $Y_{1-x}Ca_xBa_2Cu_4O_8$ ($x = 0.05, 0.1$) starting with $Ca(NO_3)_2 \cdot 4H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$–acetone and CaO, respectively. For calcium-substituted samples using $Ca(NO_3)_2 \cdot 4H_2O$, the splitting of the reflection peaks of 0 1 7 and 1 1 1 decreases severely with increasing calcium content, which has not been previously reported for calcium-substituted Y124. For samples prepared from acetone-dissolved $Ca(NO_3)_2 \cdot 4H_2O$, the XRD spectrum is much closer to the patterns

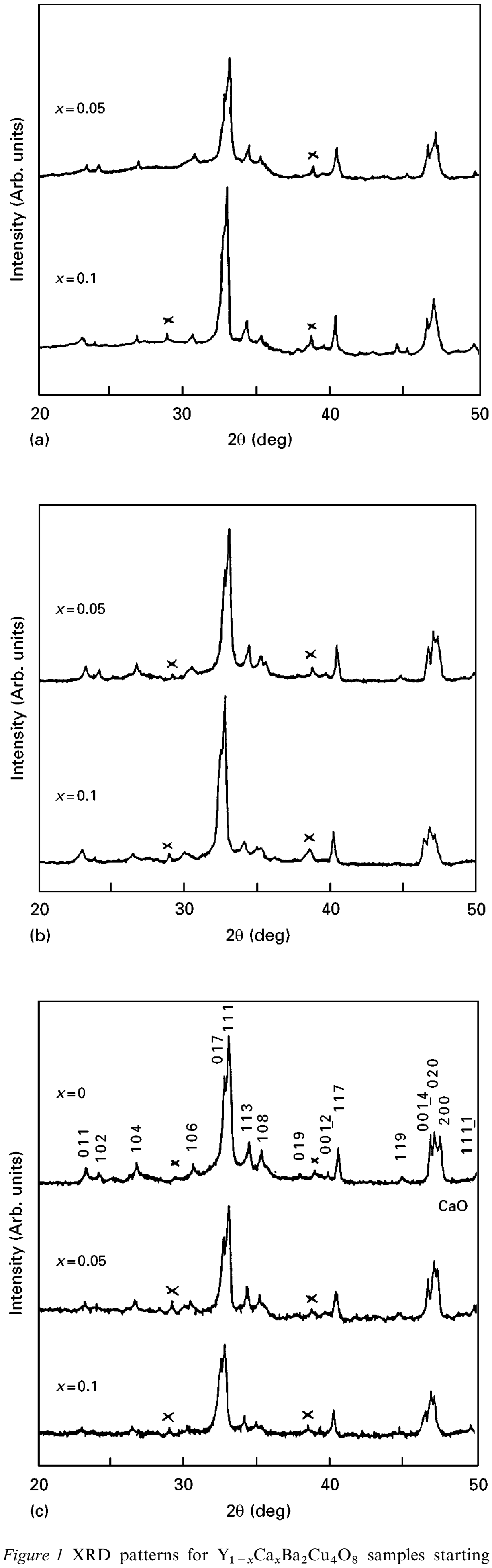

Figure 1 XRD patterns for $Y_{1-x}Ca_xBa_2Cu_4O_8$ samples starting from (a) $Ca(NO_3)_2 \cdot 4H_2O$ (b) acetone-dissolved $Ca(NO_3)_2 \cdot 4H_2O$ and (c) CaO.

reported for Y124 but the decreased splitting of the reflection peaks of 0 1 7 and 1 1 1 is still clearly seen. Nevertheless, the $x = 0$ sample and the calcium-substituted samples using dried CaO show the characteristic 124 spectra reported by Marsh *et al.* [2] and Miyatake *et al.* [6] with only weak impurity lines (marked by x). No trace of the Y123 phase is found. The lattice parameters are derived to be $a = 0.385$ nm, $b = 0.387$ nm and $c = 2.721$ nm for the sample of $x = 0$. With x increasing to 0.05 and 0.1, a and b remain unchanged while c slightly increases to 2.725 nm and 2.724 nm, respectively. The slight increase in only the c axis due to calcium substitution was reported in recent research work for samples prepared under high pressures and at ambient pressures ($a = 0.3842$ nm, $b = 0.3863$ nm, $c = 2.719$ nm for $x = 0$, $a = 0.3841$ nm, $b = 0.3863$ nm, $c = 2.721$ nm for $x = 0.05$, $a = 0.3841$ nm, $b = 0.3864$ nm, $c = 2.721$ nm for $x = 0.1$ [6]; $a = 0.3839$ nm, $b = 0.3865$ nm, $c = 2.7222$ nm for $x = 0$, $a = 0.3838$ nm, $b = 0.3863$ nm, $c = 2.7238$ nm for $x = 0.05$, $a = 0.3839$ nm, $b = 0.3864$ nm, $c = 2.7241$ nm for $x = 0.1$ [24, 27]), and could be considered a result of calcium substitution for yttrium because the ionic radius for Ca^{2+} ($r = 0.099$ nm) is larger than that of Y^{3+} ($r = 0.093$ nm). The splitting of the reflection peaks due to 0 1 7 and 1 1 1 is clearly seen for all samples, showing the orthorhombicity is not decreased with calcium substitution.

Fig. 2 shows the TG result for the 124 samples. For samples starting from $Ca(NO_3)_2 \cdot 4H_2O$, especially for that of $x = 0.1$, a remarkable weight decrease around 500 °C (a characteristic behaviour of Y123 due to the decrease of oxygen content [40]), was observed. The characteristic weight decrease, although much reduced, was still clearly seen in the $x = 0.1$ sample using $Ca(NO_3)_2 \cdot 4H_2O$–acetone. However, good thermal stability up to 800 °C was confirmed for the $x = 0$ and the calcium-substituted samples using dried CaO. The absence of the weight drop around 400–500 °C in the latter samples indicates that they do not contain Y123. It is seen that the initial calcium compound has a considerable influence on the sample quality. From the experimental results, it is apparent that H_2O in the calcium compound $Ca(NO_3)_2 \cdot 4H_2O$ has a bad influence on the formation of

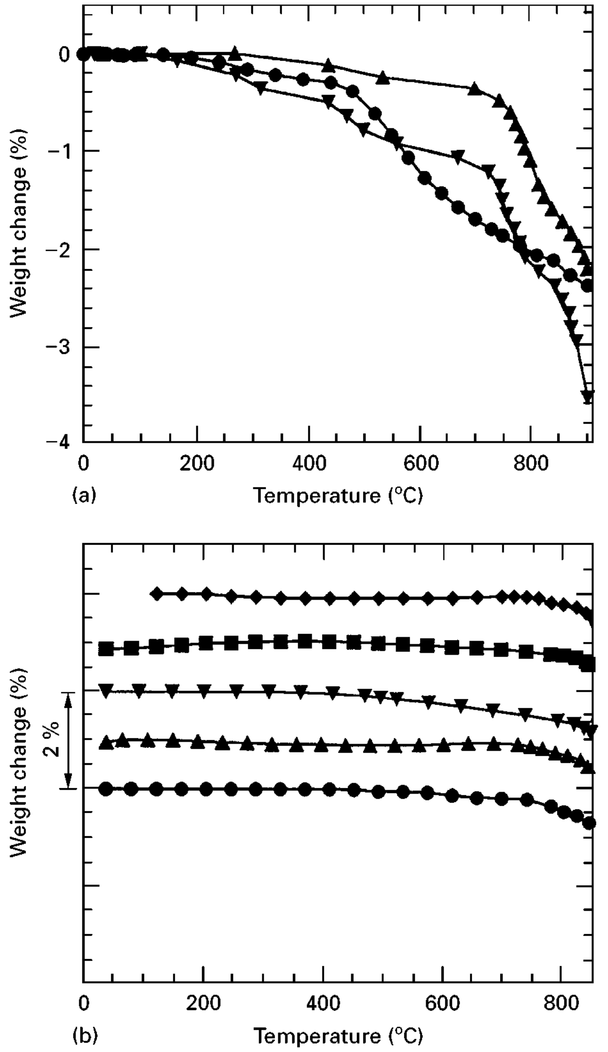

Figure 2 (a) Weight change for $Y_{1-x}Ca_xBa_2Cu_4O_8$ samples starting from (▲, ▼) $Ca(NO_3)_2 \cdot 4H_2O$ (▲, $x = 0.05$; ▼, $x = 0.1$) and (●) a Y123 sample. The arrow shows the turning point where oxygen content begins to decrease rapidly in Y123. (b) Weight change for $Y_{1-x}Ca_xBa_2Cu_4O_8$ samples starting from acetone-dissolved (▼, ■) $Ca(NO_3)_2 \cdot 4H_2O$ (▼, $x = 0.1$; ■, $x = 0.05$), and (●, ▲) CaO (●, $x = 0.1$; ▲, $x = 0.05$). (◆) $x = 0$.

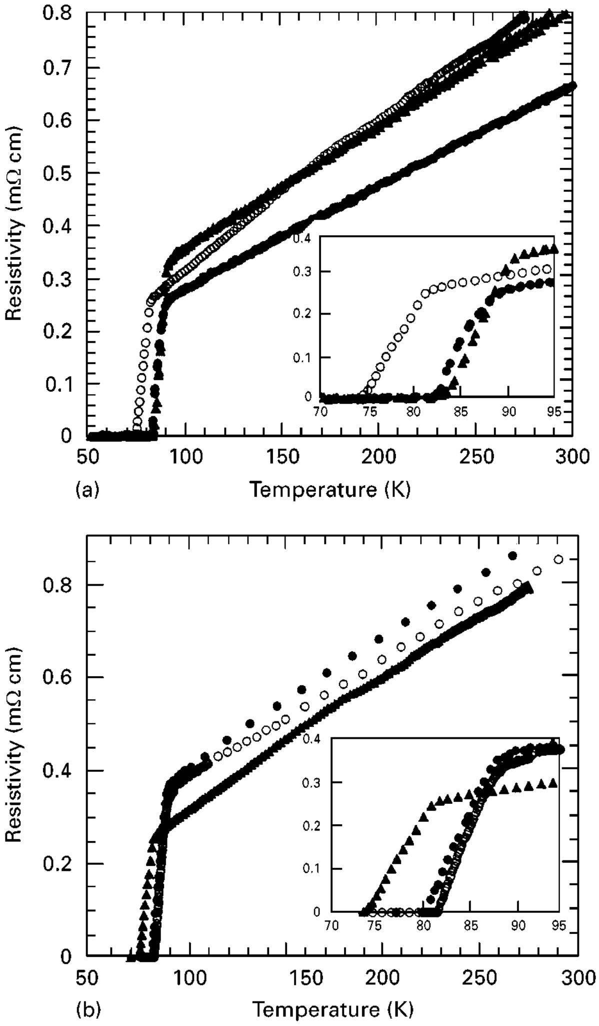

Figure 3 Temperature dependence of electrical resistivity for $Y_{1-x}Ca_xBa_2Cu_4O_8$ samples starting from (a) acetone-dissolved $Ca(NO_3)_2 \cdot 4H_2O$ ($x =$ (○) 0, (●) 0.05, and (▲) 0.1. (b) CaO ($x =$ (○) 0.1, (●) 0.05, (▲) 0).

$Y_{1-x}Ca_xBa_2Cu_4O_8$. As the reason for the improvement by using acetone-dissolved $Ca(NO_3)_2 \cdot 4H_2O$, it is thought there is a reduced water content during evaporation of acetone. For further investigations, only the results on samples from acetone-dissolved $Ca(NO_3)_2 \cdot 4H_2O$ (hereafter simply denoted $Ca(NO_3)_2$ in the following figures) and CaO were discussed.

Fig. 3 shows the temperature dependence of the electrical resistivity for $Y_{1-x}Ca_xBa_2Cu_4O_8$ ($x = 0.05, 0.1$) starting with $Ca(NO_3)_2 \cdot 4H_2O$–acetone and CaO, respectively. T_{c0} was 74, 82 and 83 K, respectively, for $x = 0$, 0.05 and 0.1 with the series using $Ca(NO_3)_2 \cdot 4H_2O$–acetone. With CaO, T_{c0} was 80.5, 82 K, for $x = 0.05$ and 0.1, respectively. The higher values of T_{c0} for samples starting with $Ca(NO_3)_2 \cdot 4H_2O$–acetone may be due to the inclusion of Y123 phase, which can produce an apparently higher T_{c0}.

Inclusion of the 123 phase may have a significant influence on the resistivity-derived T_c, therefore careful investigation of susceptibility is demanded. Fig. 4 shows the Meissner susceptibility data for $Y_{1-x}Ca_xBa_2Cu_4O_8$ with $Ca(NO_3)_2 \cdot 4H_2O$–acetone and CaO, respectively. The diamagnetic signal of samples of $x = 0$, 0.05 and 0.1 appeared at 82, 91 and 91 K, respectively, for samples using $Ca(NO_3)_2 \cdot 4H_2O$–acetone. Meanwhile, with samples using CaO, the diamagnetic signal appeared at 88 and 90 K, respectively, for $x = 0.05$ and $x = 0.1$. The latter T_c values are in good agreement with the values T_c (onset) (89 and 91 K, respectively) of oxygen-HIP processed samples [6]. This progressively enhanced T_c (onset) due to calcium content suggests that it is a direct effect due to calcium substitution.

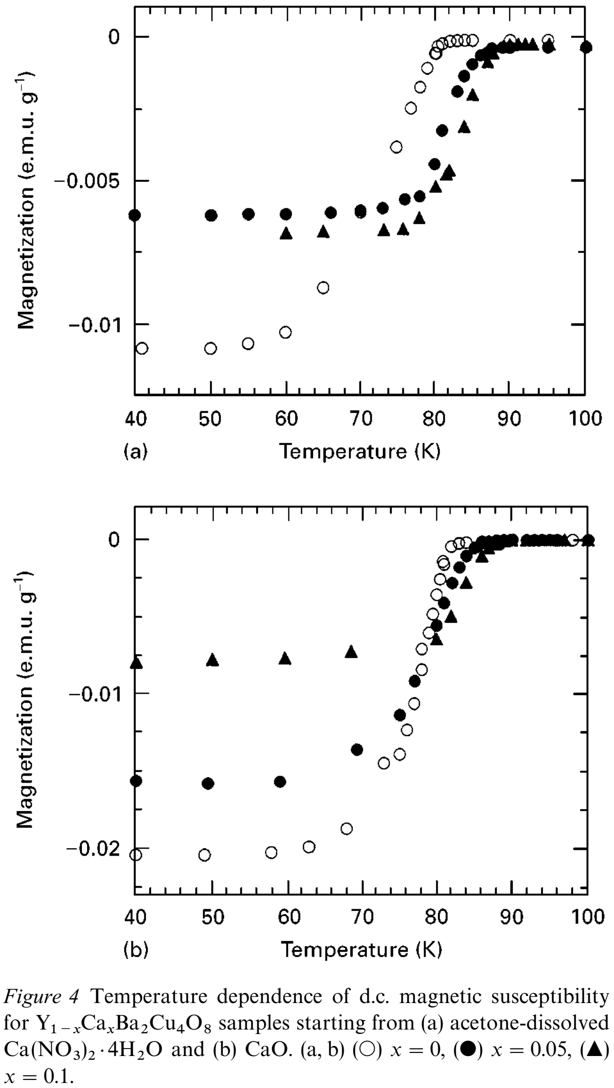

Figure 4 Temperature dependence of d.c. magnetic susceptibility for $Y_{1-x}Ca_xBa_2Cu_4O_8$ samples starting from (a) acetone-dissolved $Ca(NO_3)_2 \cdot 4H_2O$ and (b) CaO. (a, b) (○) $x = 0$, (●) $x = 0.05$, (▲) $x = 0.1$.

In summary, calcium-substituted Y124 superconductors in ceramic form were prepared at ambient oxygen pressure by a solid-state reaction method using CuI as the starting material. Several kinds of calcium compounds were used to make the calcium substitution. It was found that the state of the initial calcium compound is critical to a successful synthesis. High-purity $Y_{1-x}Ca_xBa_2Cu_4O_8$ could be prepared at ambient oxygen pressure by the present method using CuI and dried CaO as the starting materials. The zero-resistance T_{c0} values are several degrees Kelvin lower than those values exhibited by the high-temperature, high-oxygen-pressure processed samples ($T_{c0} =$ 87.4 K [6, 7], 85.5 K [8] for $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$), where the high-temperature sintering reduces the weak coupling between grains and thus achieves a narrower transition. Nevertheless, the present T_{c0} is close to that of the solution-based method (85 K [24, 37]), and much higher than that of Ag_2O doping (77 K [38]) which also uses a solid-state reaction. The present work suggests that water content present in the starting materials prevents calcium from doping into Y124.

4. Conclusion

The 124 high-T_c superconductor $Y_{1-x}Ca_xBa_2Cu_4O_8$ was synthesized at ambient oxygen pressure by a novel solid-state reaction process. A detailed investigation of the resistivity, susceptibility, XRD and thermo gravimetry showed that high-quality $YBa_2Cu_4O_8$, as well as the 90 K superconductor $Y_{1-x}Ca_xBa_2Cu_4O_8$, can be prepared by the present solid-state reaction method. It was also shown that the initial state of the calcium compound affects the calcium-substitution.

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